MULTIDIRECTIONAL WEAR AND TRANSFER FILM FORMATION IN POLYETHERETHERKETONE

A Thesis

by

KEVIN ANDREW LAUX

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2012

Major Subject: Mechanical Engineering

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Approved by:

Chair of Committee,	Christian Schwartz
Committee Members,	Hong Liang
	James Batteas
Head of Department,	Jerald Caton

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ABSTRACT

Multidirectional Wear and Transfer Film Formation in Polyetheretherketone. (May 2012)

Kevin Andrew Laux, B.S., University of Illinois at Urbana Champaign

Chair of Advisory Committee: Dr. C. J. Schwartz

Polyetheretherketone (PEEK) is a designation given to materials of the polyaryletherketone family having a characteristic distribution of ether and ketone groups in the polymer backbone. PEEK materials have high strength and chemical resistance as well as very high melting points and glass transition temperatures. Because of this combination of properties, PEEK materials find use for wear application in extreme environments where they provide a light-weight and corrosion resistant bearing material that often does not require lubrication. An initial study focused on determining the effects of supplier and molecular weight on the wear of particular PEEK materials, in addition to the effect of contact pressure. This work is significant because it highlights the fact that tribologically relevant polymers, such as PEEK materials, vary greatly in terms of their polymer morphology and processing history, and this variation must be recognized by investigators when reporting wear data.

Because of their light weight, chemical resistance, and self-lubricating properties, polymers are used in applications ranging from biomedical to aerospace. Some polymers exhibit significant differences in wear resistance based on whether they are in unidirectional or multidirectional sliding. Shear induced polymer chain orientation is

believed to be responsible for this behavior. Polyetheretherketone (PEEK) has excellent wear resistance, but its multidirectional sliding behavior has not been thoroughly investigated. A factorial multidirectional pin-on-plate wear study of PEEK was conducted with a focus on molecular weight and sliding path directionality. These factors were studied for their correlation to overall wear performance. Additionally, transfer film thickness was measured at locations along the wear path using white light interferometry. A result of this work has been a greater understanding of PEEK wear mechanisms in various sliding configurations and how they relate to transfer film formation. A major outcome was the development of a quantitative metric to describe transfer film thickness and continuity. It was found that thinner more continuous transfer films form under sliding conditions that change direction rather than overlapping along the same path. The thinner more continuous transfer film was found to also correspond with statistically lower wear behavior. Scanning electron microscope (SEM) investigation of the transfer film and pin wear surface confirmed the relationship between transfer film quality and wear.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Schwartz, and my committee members, Dr. J. Batteas and Dr. H. Liang, for their guidance and support throughout the course of this research. Their guidance in conducting meaningful research is a lesson I will take with me throughout my career.

The number of people that have thanklessly helped me throughout this work is by far too numerous to remember, but I will try my best. I would like to thank my lab mates Kevin Plumlee and Matt Darden for their advice and listening to my ideas. I would especially like to thank Mr. Plumlee for his willingness to train me in the field of tribology and to share knowledge he has gained though his course of study. I would like to thank Dr. H.J. Sue for access to his facilities and his students for allowing me use of their time and equipment. I would like to thank the Texas A&M microscopy center, especially Dr. Mike Pendleton and Ann Ellis. Only with their advice and patience in training was I able to obtain high quality images. Additionally, I thank the members of the APPEAL consortium for financial support during this research and the faculty members for their advice and keen insights.

Finally and most importantly I thank my parents Frank and Diana Laux. Their unwavering love and support has enabled me to achieve whatever it is I set my mind to.

NOMENCLATURE

PEEK	Polyetheretherketone
PTFE	Polytetraflourethylene
PPS	Polyphenylenesulfide
UHMWPE	Ultra-High Molecular Weight Polyethylene
COF	Coefficient of Friction
M_w	Molecular Weight
PDI	Polydispersity Index
μm	Micrometers
m	Meters
MPa	Mega Pascals
GPa	Giga Pascals
SEM	Scanning Electron Microscope
DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical Analysis
GPC	Gel Permeation Chromatography
MLE	Maximum Likelihood Estimation
PDF	Probability Density Function
ANOVA	Analysis of Variance

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1. INTRODUCTION TO POLYMER TRIBOLOGY AND INVESTIGATION METHODS

1.1 Background on Wear and Transfer Films

Tribology is the study of the dual phenomena of wear and friction that result when materials move during contact with one another. Many applications required low friction and low wear. To achieve these goals, oil or other liquid lubricants are often used to reduce the coefficient of friction (COF) and lower wear rate. When liquid lubrication is not possible, it is common to use solid lubricants like graphite and MoS_2. These solid lubricants benefit from their ability to form a low COF tribofilm, or transfer film, against their mating surface. The film also serves as a barrier between the dissimilar materials and reduces the abrasive wear on the bulk materials. Similarly, several polymers such as PTFE, PPS, and PEEK have the ability to form transfer films. Unlike graphite and MoS_2 that form films because of their weakly bound layered structure, the exact mechanism for polymer transfer film formation is not known.

The presence of a transfer film in polymer wear is often associated with low friction and low wear rates. Although this is generally true, it does not apply under all conditions and low wear and low friction do not always go hand in hand. For instance, PTFE has exceptionally low friction (COF~0.1) but overall poor wear resistance. Additionally, polymer viscoelastic behavior changes with the temperature, loading, and presence of solvents, so prediction of when films form is inexact. Historically, fillers

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This thesis follows the style of *Wear*.

have been added to polymers for various reasons including improvement of their mechanical properties and reduction of wear. The addition of inorganic fillers and polymers that aid in transfer film formation has been shown to also be an effective method for reducing wear. Because they can both help compartmentalize damage and chemically promote film adhesion, filled polymers can achieve high wear resistance while maintaining comparable coefficients of friction. However, adding fillers may not be the only method for engineering a polymer to suit a particular bearing application. Improving polymer mechanical properties also shows promise. Some properties are dependent upon the molecular weight, crystallinity, and entanglement density, which change depending on the grade and processing history. Such variation across the range of properties means performance cannot be predicted based primarily on polymer type. This is an area of polymer tribology that has neither been well investigated or understood. Furthermore, the wear resistance and transfer film formation will depend upon the composition of the counterface. In theory, the counterface should be hard enough to resist deformation by the polymer and sufficiently smooth to reduce abrasion from asperities, but rough enough to promote anchoring of transfer films. However, even this simple concept is not fully supported due to the myriad of wear mechanisms as well as chemical and thermal interaction between the polymer and counterface. It has been found that an "excessively smooth" counterface can result in significantly worse wear and friction as a result of a melting type of wear and poor transfer film adhesion[1]. No predictive models exist that indicate if a transfer film will deposit on a particular counterface let alone the resulting wear.

1.2 Experimental Setup

Because of the complexity of tribological behavior, empirical investigations are necessary to understand phenomena and make progress in the field. This very often requires the construction of specialized test equipment. One very common method of wear testing involves the use of a pin on disk setup where a polymer pin is loaded against a rotating counterface. Although such a wear test can produce meaningful results, the in-service performance of the polymer often does not correlate well with laboratory results. A further complication in the work is the substantial statistical variation in results. This mandates the copious use of replications in order to attain the statistical power required for hypothesis testing. Therefore it is up to the engineer to design a test rig that can both accurately simulate wear and can accommodate multiple samples[2, 3]. One issue with the study of polymer wear is that the polymer chains have the ability to orient themselves in the direction of the applied stress. This phenomenon is particularly pronounced in artificial hips where the service life is orders of magnitude less than the lab tested performance[4]. One solution is to use a stage that has two independent axes of motion and counterfaces with directional surface roughness shown in Figures 1, 2. As part of the research undertaken in this work, a multi axis tribometer was configured to test PEEK samples. The wear tester ultimately has two functional requirements that were integrated into the design. First, the machine must be capable of generating pressures and velocities that will produce measureable wear. Additionally, there must be a way to record the frictional force generated at the wear interface throughout the duration of the test. As shown in Figure 2, the wear tester has four

independent stations with pneumatically controlled pistons. Each station can hold a 0.25 inch diameter pin which is loaded against a counterface. The counterfaces move relative to the pins as the stage moves in a specified path at a programmed speed. Friction is measured using a three axis piezoelectric force sensor (Kistler) mounted on one of the stations. The force sensor is monitored by a computer throughout the test.

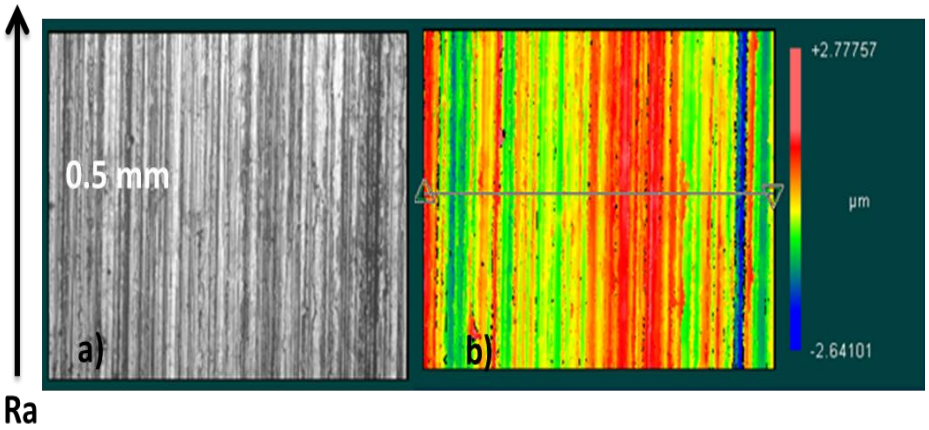


Figure 1. Surface roughness measurement of hardened D2 steel counterfaces. Arrow shows the direction of surface roughness. The image dimension is 0.5mm by 0.7mm.

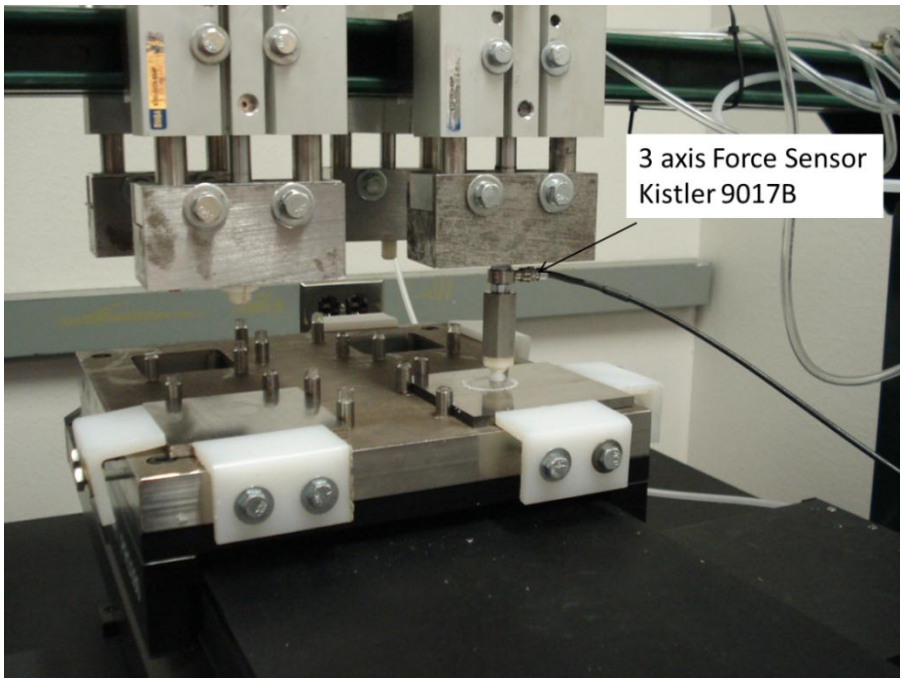


Figure 2. Multi Axis Tribometer Table with four independent test stations

1.2.1 Pressure Velocity (PV) confirmation

Because of PEEK's inherent wear resistance, testing must be done at relatively high pressures and velocities. The pressure velocity product (PV) used for typical pin on disk (POD) tests of PEEK is typically from 0.5-2 MPa*m/s[5, 6]. These values for (PV) are often achieved using substantially high velocities, 1-2 m/s, and pressures below 1MPa. Although the linear stages used in the multi-axis tester are capable of moving at speeds above 1 m/s, they cannot continuously move in tandem at such speeds. A confirmation test was performed to indicate the operating velocity range for continuous movement. A test program was written for movement in circles with a diameter of 20mm over a total distance of 100m. The velocity was checked by programming the stage to move at a desired speed and then measuring the time it takes to move the

specified 100m. It was found that the programmed speed matched the recorded speed, but the motors generate encoding errors at speeds above 400 mm/s. These faults occur because the motors cannot cooperatively move quick enough to achieve the programmed motion. For this reason, wear testing is limited to speeds in the range 300-350 mm/s for circular motion.

Since the pins are only 0.25 inches in diameter, a large contact pressure can be produced using a reasonably small load. Therefore, the limits on velocity do not significantly impact the ability to conduct wear tests. The test constraints on contact pressure were checked by recording the maximum available load. Load is applied to the pin by a pneumatically controlled piston with a bore cross sectional area of 484mm^2. Since the maximum available pressure from laboratory supplied compressed air is 80 psi, the maximum load in theory should be 60 pounds. Therefore, the maximum contact pressure for PEEK is about 8.5 MPa using Hertzian assumptions. The loads applied to the sample pins were checked for each of the four pistons using a thin film single point force sensor (FlexiForce). The loads were checked at five operating pressures and compared to the expected load based on the piston bore area as shown in Figure 3. All four pistons produced a load that is 5 lbs. greater than expected, but this difference was attributed to the free hanging weight of the pneumatic piston and sample holder.

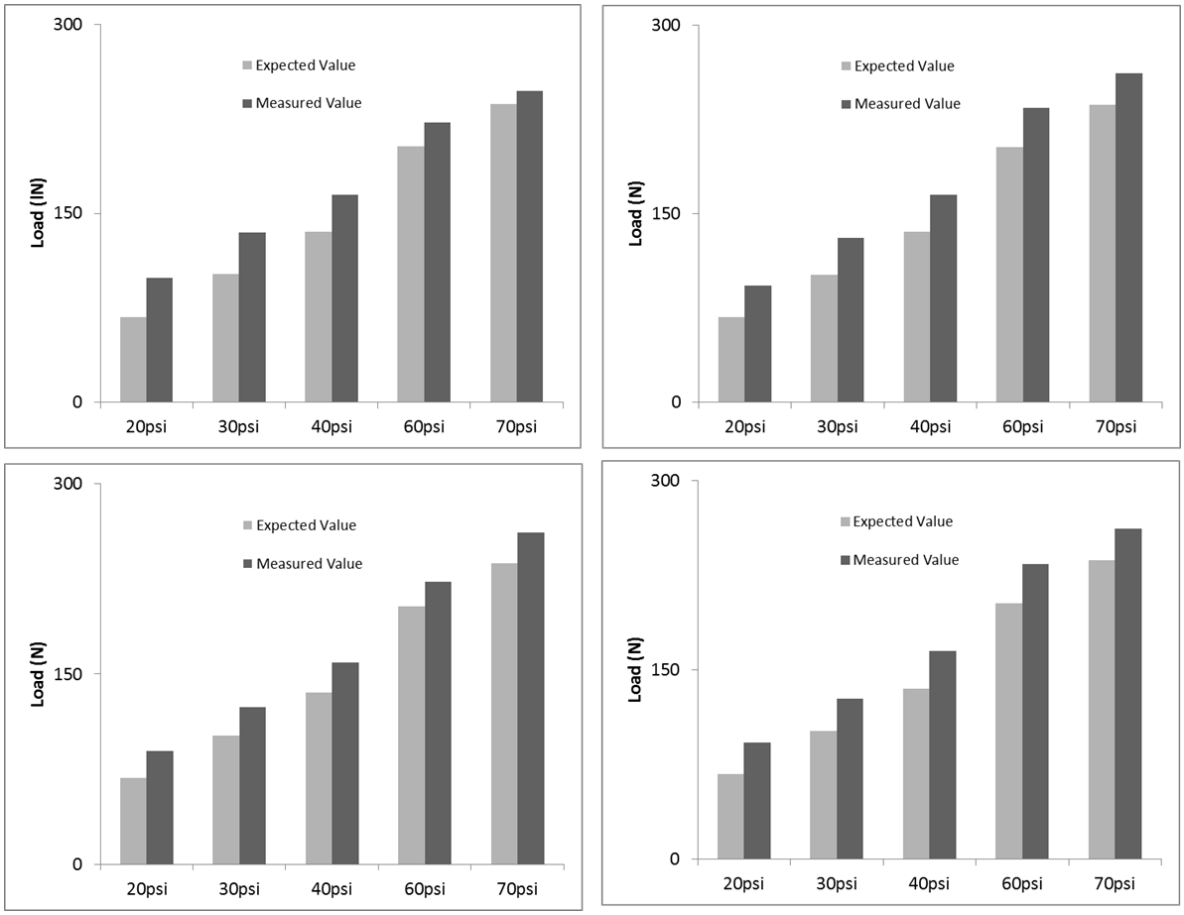


Figure 3. Measured and expected loads for each of the four pneumatic pistons

1.2.2 Wear Confirmation

In order to achieve meaningful wear results, the recorded data must be reproducible between each test and at each of the four test stations. It is also necessary to know at what point steady state wear is achieved. Wear in polymers will typically go through an initial period where debris is quickly generated followed by a period of more gradual steady wear. Since the primary objective of wear testing is to predict the in-service life of a material, it is necessary that testing is long enough to attain steady state. An initial screening experiment was performed using samples finished to 0.2µm Ra on

the wear surface. Four tests were conducted for a sliding distance of 3km at a speed of 300 mm/s and a contact pressure of 3.9 MPa. The samples were weighed before and after each test and the same four sample pins were rotated between each of the test stations. This confirmed that the results were repeatable between each of the test stations. The volumetric wear for each station averaged across the four tests is shown in Figure 4. The standard deviation of testing showed no difference in runs.

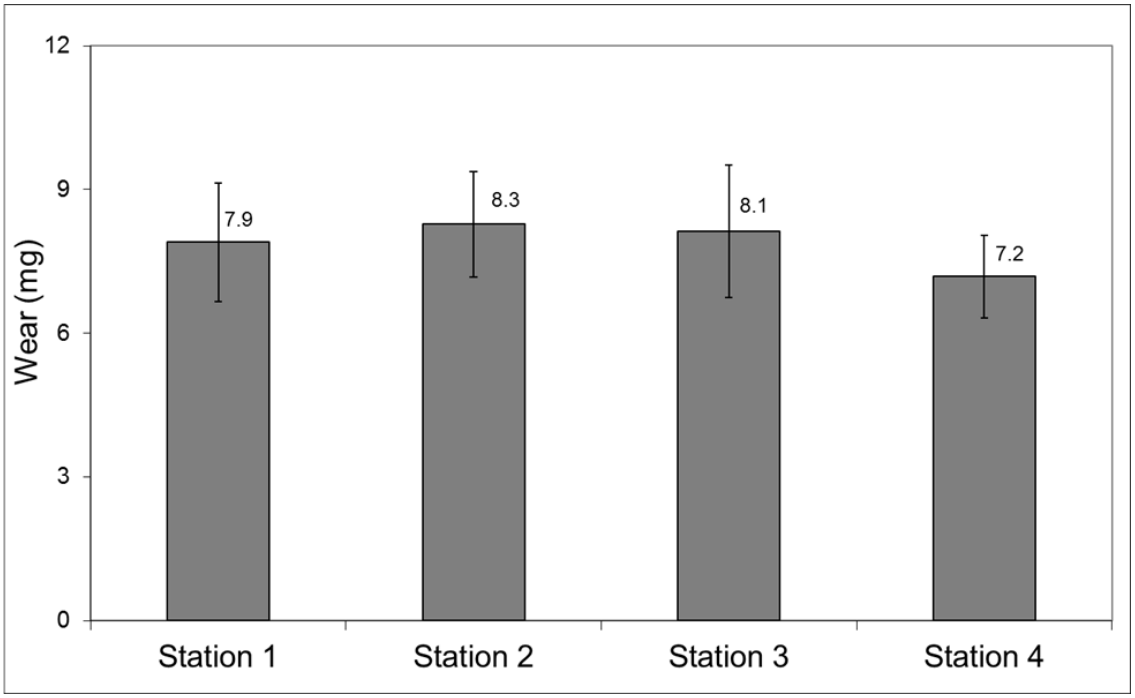


Figure 4. Wear results from initial screening experiment sample size (n=4)

2. EFFECTS OF CONTACT PRESSURE, MOLECULAR WEIGHT, AND SUPPLIER ON THE WEAR BEHAVIOR AND TRANSFER FILM FORMATION OF POLYETHERETHERKETONE

2.1 Introduction

Polyetheretherketone (PEEK) is a type of aromatic-backbone polymer belonging to the polyaryletherketone (PAEK) family of thermoplastics. PEEK materials demonstrate high strength, stiffness, and toughness along with excellent chemical resistance in many applications. These materials find widespread use in high temperature applications because of their very high glass transition temperatures, often in excess of 140°C [7]. Crystallinity, which has a significant impact on PEEK's mechanical properties and chemical resistance, is typically from approximately 30 to over 40 percent, based on polymer morphology and processing methods [8]. There are many variants within the family of PAEK materials, and they are named according to the presence of ether and ketone units in the backbone. Polyetherketone (PEK) and polyetherketoneketone (PEKK) are examples. Though often overlooked, there are wide variations in the molecular morphology among polymers classified as PEEKs, because of the varied approaches to polymerization chemistry and processing. Various grades of PEEK in their neat form have been shown to have good tribological and wear properties, possibly due to high strength, modulus, and toughness.

Polymers such as PEEK, polyphenylenesulfide (PPS), polytetrafluorethylene (PTFE), and ultra-high molecular weight polyethylene (UHMWPE), find use in extreme environments where the use of traditional metal bearing materials and fluid lubricants

are impractical [9-11]. These polymers typically exhibit an acceptably low coefficient of friction (COF), and they often deposit a transfer film on a mating metallic counterface. It is hypothesized that the film protects the bulk polymer from direct abrasive wear by the harder counterface. The mechanical, thermal, and chemical causes for this film deposition in PEEK and its effect on wear have been studied by several researchers. Briscoe et al. [12] conceptualize the wear polymer surface during sliding to be two separate regions. An interface region with a depth of 100 nm has been proposed that is responsible for adhesive friction forces and a cohesive region that dissipates the frictional work through viscoelastic response. It is thought that the mechanical and thermal interaction of these two regions plays a primary role in wear debris generation and film formation. In thermoplastic polymers, such as PEEKs, the frictional heating that arises at the interface is enough to cause a significant drop in the storage modulus. Analysis of PEEK wear debris by Zhang et al. has shown a drop in crystallinity and interfacial temperatures above melting that may promote plastic flow [13]. Studies of amorphous PEEK films, however, have shown that temperatures above the crystallization temperature are reached and the storage modulus may increase from friction induced crystallization [14]. When the counterface has sufficient surface roughness, material can be removed from the polymer bulk through cutting and abrasion by the asperities. Counterface roughness is likely one of the dominant wear factors in both filled and unfilled polymers and has been studied by Blanchet et al. [15], among others. Hollander et al. [16] developed an average asperity radius model to explain the relation between roughness and wear. Their proposed model states that transfer film

formation is aided by entrapment of wear debris between asperity contacts. There appears to be a transition point in surface roughness above which the transfer film is unable to fully protect the bulk polymer from the abrasive action of the counterface, resulting in increased wear [17]. Additionally, material removal during wear does not necessarily mean that a film will form since there must also be adhesion to the counterface. There is evidence to suggest that film adhesion occurs because of entrapment of particles between asperities, localized melting, and chemical bonding. Polymer wear performance is often discussed in terms of the wear in response to product of pressure and velocity, or PV. Because pressure and velocity can act synergistically, bearing materials are often assigned a PV limit above which loads cannot be sustained due to excessive wear and frictional heating. Zhang and Schlarb showed that at calculated normal pressures above 4 MPa, the cutting wear mechanism vanishes and there is evidence of plastic flow at the wear interface of PEEK [18]. Additionally, excessive velocity will strongly influence heating at the surface and cause debris aggregation that may disrupt film deposition [6, 19]. Though surface roughness and thermal factors strongly affect wear, polymers have been shown to form thick adherent transfer films when these factors are absent. In early work by Jain and Bahadur, the sliding wear between two different polymer surfaces indicated that the cohesive energy density of the two surfaces contributed to material transfer. They found that in sliding friction, material is transferred from the polymer surface of lower cohesive energy density to the one with greater cohesive energy density [20].

Despite numerous studies of polymer wear and transfer film formation, no model currently exists to precisely predict wear a priori. This is due to the complexity of the wear phenomenon and its combination of activity of many parameters. The viscoelastic nature of polymers deems that mechanical properties will change as a function of time and temperature. Couple this fact with the inexact knowledge of the temperature and stress distribution at the wear interface and it indicates that the problem is still not well understood. Furthermore, there is no definitive metric for what constitutes a good transfer film. Historically, PEEK films have been described as thick, uniform, and continuous relative to other polymers. Because of these subjective and qualitative descriptions, it has been challenging to understand the relationship between transfer film characteristics and wear. Very little conclusive work regarding transfer film height as it relates to wear volume has been done.

The purpose of this study was to explore the amount that wear and transfer film formation of various PEEKs varies with respect to different polymer morphologies and sliding conditions. In contrast to much of the earlier work in the area, PEEK is not assumed to be a unified homogeneous material, but rather a family of materials that have differences in molecular weight and dynamic mechanical properties with respect to the polymerization process used by different suppliers. Furthermore, the effect of normal load with respect to polymer morphology was examined. The investigation included wear testing conducted using a novel multi-directional pin-on-plane tribometer. Transfer film height was measured using white light interferometry to determine if a direct relationship exists between wear and transfer film height in PEEK materials. The

significance of this work is not only the tribological data, but also the fact that extensive analyses were performed to fully understand the morphology of the various PEEK grades that were used in the work in order to understand how they affected wear.

2.2 Materials and Methods

2.2.1 Materials

Four neat PEEK materials from two different suppliers, identified as '1' and '2', were used in this work. The identities of the suppliers are not reported due to confidentiality requirements; however morphological data is reported in order for the reader to evaluate the reported results. All samples were injection molded under controlled and constant conditions and finish machined into pins for wear testing and thin bars for dynamic mechanical analysis. Two different grades of PEEK from each supplier were used based on measured molecular weight. The grades were selected so that the 'low' and 'high' values of M_w were comparable across the two suppliers. In this paper the high molecular weight grades are referred to as '1H' and '2H' and low molecular weight grades as '1L' and '2L', respectively. Gel permeation chromatography (GPC) was used to characterize the weight average molecular weight (M_w) and polydispersity index (PDI) of each of the four materials and the results are shown in Table 1. Differential scanning calorimetry (DSC) was used to characterize the degree of crystallinity of each of the materials, and the data are also reported in the table.

Table 1. Compilation of morphological (weight average molecular weight, Mw, and polydispersity index, PDI, and crystallinity) and viscoelastic data (storage and loss moduli) for the four PEEK grades used in the study.

Sample	M_w	PDI	% crystallinity	Storage Modulus (GPa)	Loss Modulus (MPa)
1L	76306	2.76	42	3.36	71.5
2L	84709	2.64	36	3.89	121
1H	143645	3.72	35	3.07	60.9
2H	118548	3.52	32	3.72	135

2.2.2 Wear Testing

Wear pins of the four PEEK materials were molded and machined to a diameter of 6.4 mm and length of 19.1 mm. Before testing, the wear surface of each pin was finished to a surface roughness of approximately 0.2 μm Ra. Samples were ultrasonically cleaned, dried, and weighed before and after each test on a precision balance with a resolution of 0.01mg. For this work, a two-axis tribometer was employed which incorporates two programmable linear stages (Aerotech). The tribometer allows for sliding of pin specimens against planar counterfaces under an applied normal load along a specified wear path and sliding velocity. Typical pin-on-disk methods of wear testing are only capable of subjecting the polymer specimen to unidirectional sliding. It has been shown by Schwartz et al. and others that unidirectional wear testing of polymers often underestimates the wear observed in actual bearing applications by orders of magnitude[21]. It is theorized that polymer chains on the wear surface orient themselves in the direction of sliding and thus exhibit directional strengthening and subsequent increased wear resistance. Wear pins were loaded against tool steel

counterfaces using pneumatically controlled actuators and the tribometer was programmed to slide the pins in a circular path with a diameter of 20 mm for 80,000 cycles (approx. 5km total sliding distance) at a constant sliding velocity of 0.1 m/s. The test duration was chosen to be sufficiently long to attain steady state wear. Testing was conducted using applied loads of 60 N (low) and 125 N (high), which resulted in Hertzian calculated pressures of 1.8 MPa and 3.9 MPa, respectively. Hardened D2 tool steel counterface plates (HRc 56.6 measured) were ground so that roughness was oriented in one direction with an average roughness Ra of 0.5 μm. Since the wear path was circular, the angle between the direction of the pin motion and the counterface roughness direction was constantly changing. The change in mass was recorded and the reported density of the respective PEEK materials was used to calculate volumetric wear. Wear testing followed a full factorial experimental plan with factors including normal load, polymer molecular weight, and polymer supplier. A total of four pins of each material were tested in randomized order to account for statistical variation.

2.2.3 Transfer Film Measurement

Transfer films have traditionally been assessed from a qualitative standpoint and therefore objective metrics related to the bonding, thickness, and uniformity of films has not been well reported. A goal of this work was to develop a quantitative measurement technique to compare transfer films formed by different PEEK grades. Optical microscopy was used to give information about film uniformity. A white light interferometry based profilometer (Zygo) with analysis software was used to measure

the film thickness at locations along the wear path. The circular sliding path was indexed at 45° angular increments and film thickness was measured at these locations. The profilometer produced a topographic map for both the film and underlying counterface for more detailed examination of film continuity where required.

2.2.4 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) allows for the characterization of a material's viscoelastic behavior by measurement of the storage and loss moduli of the material across a range of temperatures and loading frequencies. Thermoplastic polymers undergo transitions from glassy to rubbery at a temperature known as the glass transition temperature, T_g. This transition was found with DMA for the materials by locating a drop in storage modulus and a peak in the trigonometric tangent of the phase lag between the applied stress and material response, referred to as 'tan δ'. Storage modulus indicates the elastic stiffness component of a material when subjected to a load, while the loss modulus is related to the capability of the material to damp the oscillating mechanical energy input into the sample. A simple model of the sliding wear process suggests that wear resistant materials must be able to support applied load without extensive deformation (storage modulus) but also absorb the impact produced from sliding over asperities (loss modulus). DMA (TA Instruments, RSA-G2) was performed to characterize each of the four materials and determine if any relationship existed between the wear performance of different PEEK grades and their viscoelastic properties. Testing was performed in three-point bending mode. Injection molded

samples were machined to dimensions of 40 x 11.5 x 3.3 mm in accordance with ASTM D790 [22]. A temperature sweep was performed with a ramp rate of 3°C/minute between 25 and 300°C. During the test, a 0.02% strain was applied with a loading frequency of 1 Hz.

2.3 Results

2.3.1 Wear

The results from the multidirectional wear testing of the four PEEK grades are plotted in Figures 5 and 6 for the calculated contact pressures of 1.8 and 3.9 MPa, respectively. Figure 5 shows that at the lower pressure, wear is reduced as molecular weight is increased. At high M_w, the wear of the grade from supplier 2 is roughly half of that from supplier 1. Interestingly, the variance of performance in the '2L' samples was greater than for the others. At the higher pressure, the same trend was observed with a reduction in wear resulting from an increase in molecular weight. The approximately 2:1 ratio of the wear of supplier 2 versus supplier 1 still holds at the high molecular weight. The most notable result is the large increase in the wear of the low molecular weight grade from supplier 1 compared to that of the other supplier. The results show a drastic increase in wear for grade '1L' as pressure is increased. In this latter case, variance of the wear amounts is again very large.

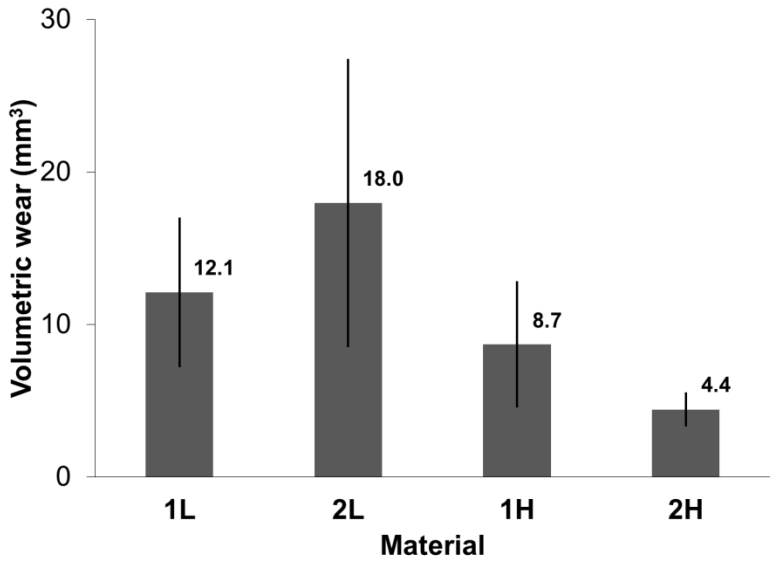


Figure 5. Wear results for the various PEEK materials after 5 km sliding distance under calculated contact pressure of 1.8 MPa. The bars indicate the size of standard error of the means (n=4).

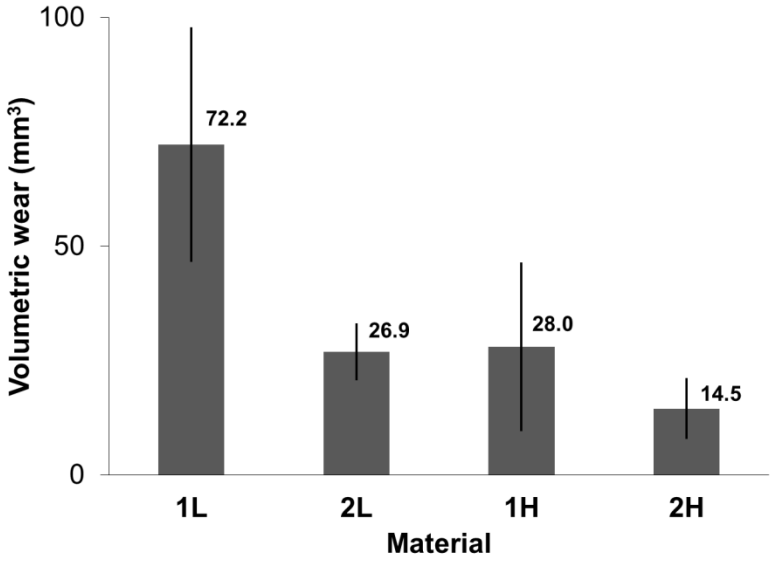


Figure 6. Wear of the various grades after 5 km sliding distance under contact pressure of 3.9 MPa.

Analysis of Variance (ANOVA) was performed on the factorial wear data to determine which, if any, of the three factors (molecular weight, contact pressure, or supplier) had a significant effect on wear behavior. The analysis showed that both molecular weight and contact pressure did indeed affect the resulting wear of the PEEK materials, with p-values of 0.009 and 0.045, respectively. Within the resolution of this experiment, the material supplier did not have a significant effect on wear amounts (p=0.113). However, the interaction between contact pressure and supplier gave indications of potentially being significant (p=0.096), as shown by the drastic effect of increased pressure on the wear of the low molecular weight sample from supplier 1.

2.3.2 Transfer Film

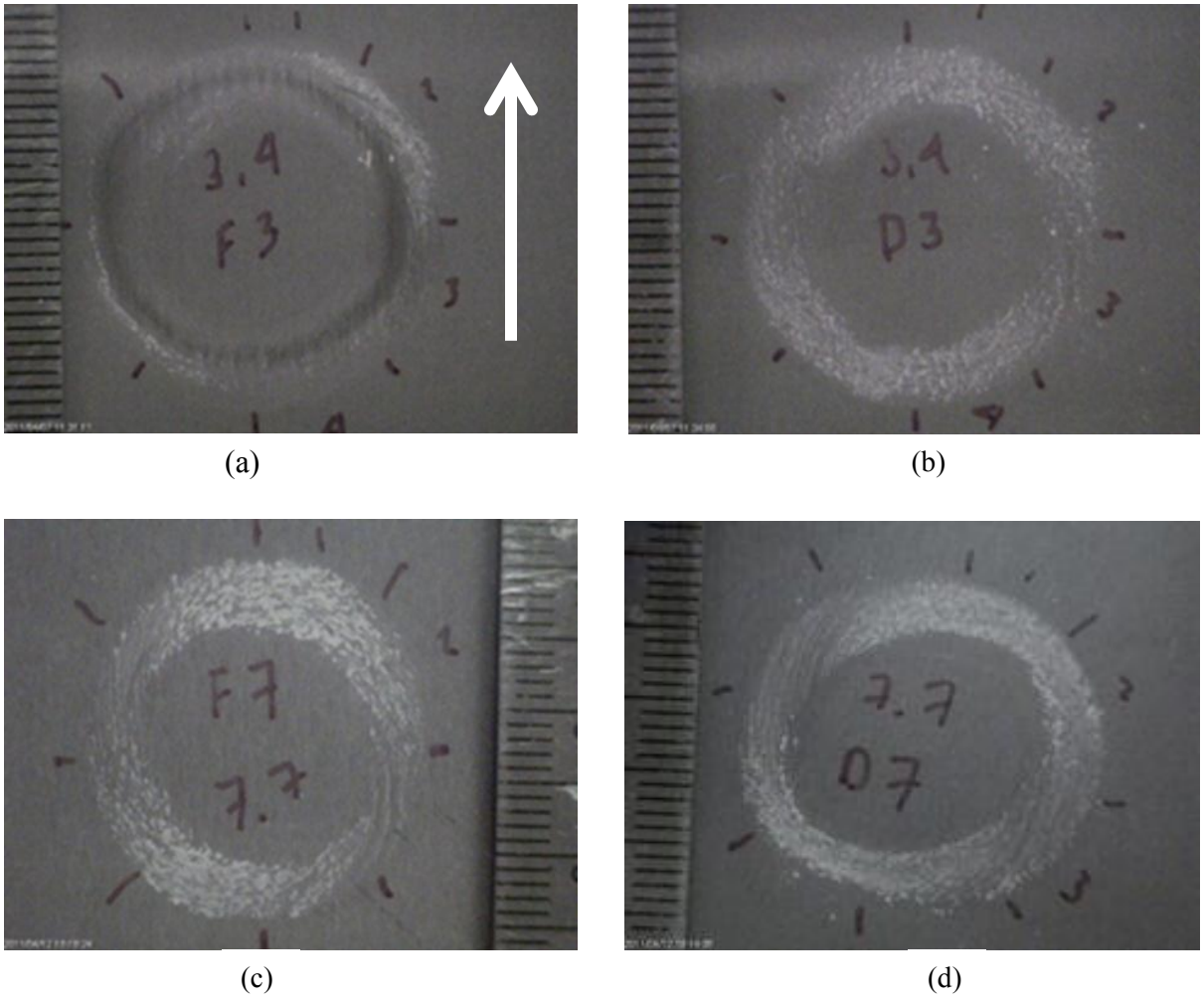
Figure 7 shows selected images of transfer films from supplier 1 at both low and high contact pressures. The results for supplier 2 were very comparable and are thus not shown here. Two things are of note in the images. The first is that thicker regions of film tend to be deposited at the top and bottom of the image, where the sliding direction of the wear pin was perpendicular to the counterface roughness direction. Films become much thinner at the locations where sliding was parallel to roughness. Secondly, there is a qualitative increase in the continuity and what looks to be thickness of the transfer films as both molecular weight and contact pressure are increased. This is most evident when comparing the low weight, low pressure film to that of the high weight, high pressure film in Figure 7(a) and (d), respectively. Another observation of note is that in Figure 7(a), the film looks to be more of a discoloration of the counterface than a

substantial deposition of polymeric material. The intermediate films Figure 6 (b) and (c), show a film that appears to be a collection of discrete lumps of material as opposed to a continuous film. In fact, these images suggest that a more precise definition of the term 'transfer film' is required, because there a different morphological characteristics apparent.

In order to determine if there was a strong relationship between average transfer film thickness and wear, data from each of the wear tests was plotted against thickness. Average film thickness was calculated using the thickness measurements from 45° increments around the circumference of each film. The resulting plot is shown in Figure 8. Two pieces of information are apparent from the data. The first is that all films had a mean thickness of at least 2 μm. It is not clear if this is a limit that is dependent on the specific properties of the PEEK materials used, or if it depends on the sliding conditions used in the study. Secondly, there does not appear to be any direct relationship between film thickness and the resulting amount of wear. This is a somewhat surprising result in light of a paradigm in the polymer tribology literature that suggest that 'thin' films lead to low wear rates. These results show that films with mean thicknesses below approximately 4 μm produce low wear, but low wear is also found in some cases with much thicker films. Another aspect of the relationship that could not be determined from this study is whether the variation in film thickness around the wear path had an effect on the wear amounts. ANOVA was performed using the thickness data for the three experimental factors and it was found that none of the individual factors had a significant effect.

2.4 Discussion

The overriding conclusion from this study is that there are very clear differences in wear behavior in PEEK with respect to sliding conditions and polymer morphology. The former aspect is routinely expected, but the latter aspect is what is most crucial for the practical uses of these materials. This study represents a well-controlled experimental investigation of various PEEK materials in a consistent manner and with very substantial knowledge of the actual polymer morphology of the samples themselves. This approach is vital to producing useful results, because the properties of polymers, including PEEKs, are highly influenced by their processing conditions. The crystallinity, entanglements, and branching can vary between grades and will contribute to significant differences in mechanical behavior. It is critical to know if such differences in mechanical behavior will contribute to a significant difference in wear behavior. Additionally, very little is known with regards to how transfer film deposition differs between different grades of the same polymer. A relation between transfer film thickness and continuity with respect to molecular weight would further explain how films form and adhered to the underlying counterface.



(a) (b)

(c) (d)

Figure 7. Optical micrograph images of transfer films for PEEK grades from supplier 1 resulting from the following sliding conditions: a) low molecular weight, 1.8 MPa; b) high molecular weight, 1.8 MPa; c) low, 3.9 MPa; and d) high, 3.9 MPa.

The first issue to consider in analyzing the wear data is why is there a very significant effect of molecular weight at low contact pressure, but less of an effect at the higher pressure. One potential explanation for this behavior may be that the primary difference between the low and high molecular weight materials for a given supplier was the assumed entanglement density of the polymer chains. Characterizing this was beyond the scope of this study, but it could account for the results observed. Typically, when entanglements are increased in a polymer, mechanical properties such as tensile strength and toughness are increased. Dynamic mechanical properties are not necessarily increased, as evidenced by the results reported in Table 1. It is surmised that with a high number of entanglements, a polymer exhibits greater tenacity when attempts are made to separate fragments from the bulk polymer. In this way, entanglement density might explain the reduced wear behavior of the high molecular weight polymers in two ways. Firstly, it becomes more difficult for the counterface asperities to remove debris from the bulk. Secondly, once material has been removed and is adhered to the counterface, the transfer film has a high mechanical integrity thus maintaining a persistent film. At the high contact pressure, ignoring the low molecular weight material from supplier 1, wear results become more comparable at the different molecular weights. Higher contact pressure may likely produce higher temperatures at the wear interface, and thus the effect of the greater number of entanglements in the high molecular weight materials might be overcome by the effects of thermal softening of the materials during wear. Interestingly, at high molecular weights, the wear of materials from supplier 2 is approximately half of that from supplier 1. This may indicate a fundamental difference

in polymer morphology in the materials beyond molecular weight. In fact, the table indicates that the molecular weight of 2H is somewhat lower than 1H. Other morphological factors that may play a role include differences in entanglement density, crosslinking, or branching. These factors were not characterized in this study but provide clues to future steps to be taken in this investigation. The only substantial difference observed between these two high molecular weight materials is that the loss modulus of 2H is approximately double that of 1H. This further suggests a morphological difference as suggested above, and very significant differences in the viscoelastic response of the materials under loading at the elevated temperatures of the wear interface.

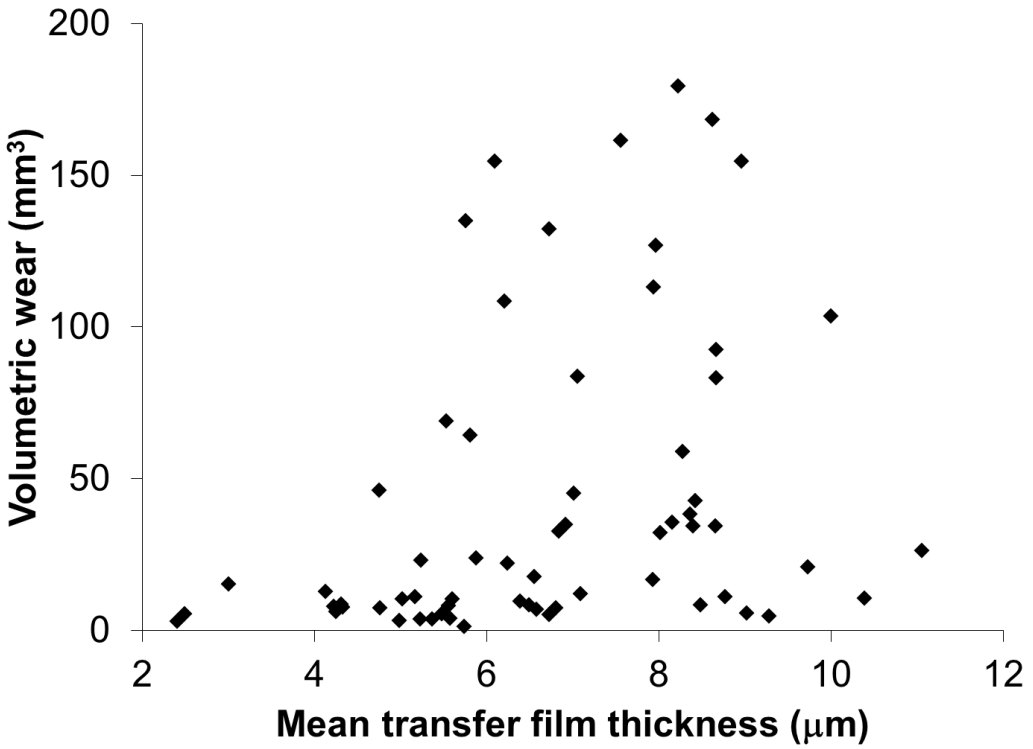


Figure 8. Plot of volumetric wear versus the mean transfer film thickness measured for the individual tests. No strong correlation exists between the parameters.

Another aspect of the wear data the bears examination is the substantial increase in the wear of material 1L when transitioning from low to high contact pressure. At the low pressure, the material has a wear amount comparable to the low weight material from the other supplier. However, the mean wear rate of 1L increases nearly six-fold as the pressure is increased. This behavior is very challenging to explain in light of any differences in entanglements or dynamic mechanical properties, as discussed above. Material 1L has the highest crystallinity of all four materials at 42%. One possible explanation for the wear behavior observed is that at low loads, the increased crystallinity has the effect of imparting wear resistance that is not present in the other three materials. At the high contact pressure, it may be that interface temperatures are high enough to anneal the surface layer of the materials, thus rendering the initial crystallinity irrelevant. Predicting temperatures at the wear interface accurately is an imposing challenge, however thermal modeling in future investigations may shed light on the presence of crystalline morphology during sliding.

Examination of the transfer films has shown that films attain their greatest thickness at the portions of the wear path where the pin was sliding perpendicular to the counterface roughness direction. On the other hand, some tests resulted in a complete lack of film in locations where sliding was parallel to roughness. The explanation for this behavior is most likely the mechanical abrasive action of the hard counterface asperities against the PEEK materials during sliding. Early in the wear process, the asperities are able to remove debris from the bulk polymer and entrap it mechanically into the grooves of the counterface when the roughness is transverse to sliding direction.

However, sliding parallel to the roughness direction likely results primarily in plowing of the polymer material without significant debris removal. As entrapped debris accumulates at the perpendicular directions, the transfer film forms as sliding continues. At steady state wear conditions, the situation may change somewhat because the hard asperities at the perpendicular directions are now covered by a soft transfer film. Another aspect of the transfer films is that as contact pressure or molecular weight are increased, the films tend to have more a smeared characteristic especially at the locations on the wear path where sliding was parallel to the roughness direction. This is especially apparent in Figure 7 (c) and (d). It is not visible at the low contact pressure condition shown in Figure 7 (a). This behavior suggests that wear interface temperatures were sufficient to cause viscous flow of the polymer face and/or the top layer of the transfer film, such that softened polymer was smeared along the wear path. Such behavior has been shown in the deposition of transfer films on low-thermal-conductivity counterfaces, such as glass, and typically results in high wear rates [23].

The final issue of consideration regarding these results is the lack of a relationship observed between mean transfer film thickness and the resulting wear in these materials. There are a few potential explanations for this lack of correlation. Firstly, it may be a weakness in the use of the average film thickness over the full circumference of the wear path. The mean takes into account all of the thickness measurements taken at 45° angular intervals, but does not account for the distribution of thicknesses. Furthermore, it is not clear at this point how to analyze films that are not continuous but are collections of discrete lumps of transferred material. Future work

will focus on developing quantitative metrics to further characterize the film in light of potential non-uniformity over the entire wear path. A second possible explanation for this result is that there is some mean thickness threshold beyond which wear is accelerated rather than reduced when a film is present. Examining the data, it is clear that film thicknesses less than approximately 4 μm coincided with the lowest wear amounts observed. Thicker films may undergo a continual process of debris removal, film deposition, and film removal. It is likely that such iterative behavior would lead to accelerated wear. A third explanation for this behavior might be that transfer films do not attain an asymptotic thickness at some steady state condition during sliding, but that their thickness may actually exhibit an oscillatory behavior as wear progresses. In the latter case, obtaining a static measure of film thickness does not reflect the true dynamic situation occurring during wear. If such behavior does happen with the PEEK materials studied here, it would be reasonable to characterize time-based measures such as a time constant or a frequency relationship to film height. These would be further parameters to consider in terms of their relationship to wear. Finally, the lack of correlation between film thickness and wear may be due to the fact that the PEEK transfer films were not smooth, continuous films but tended to be discrete patches of deposited material. It could be argued that a discontinuous film might lead to higher wear because of extreme variations at the wear interface. What remains to be investigated with these PEEK materials, is whether continuous films can be achieved under different sliding conditions, or if these materials are averse in some way to depositing uniform films.

2.5 Conclusions

The following conclusions were drawn based on the results of this study:

1. The family of PEEK materials varies widely in properties among different grades. It was shown that molecular weight played a very significant role in the wear of particular grades of PEEK.

2. The wear of these PEEK materials was significantly affected by the contact pressure during sliding, with higher pressures leading to higher wear. The change in pressure had a more drastic impact on the wear of the low molecular weight grade from supplier 1 than on the other three materials.

3. Transfer films showed their maximum thickness at the locations on the wear path where pin sliding was perpendicular to the counterface roughness orientation. Conversely, the thinnest portions of the transfer films were found when pin sliding was parallel to the roughness direction. This is likely due to a mechanical abrasion and debris anchoring mechanism.

4. Mean transfer film thickness varied from approximately 2.5 μm up to 11 μm. Mean thickness did not show a direct correlation to the wear of the PEEK materials, though it was observed that films with mean thickness of less than 4 μm correlated with materials having the lowest wear.

2.6 Acknowledgement

The authors would like to thank the members of the consortium for Advancing Performance Polymers for Energy AppLications (APPEAL) for providing the financial support and PEEK materials used in this study.

3. INFLUENCE OF SLIDING PATH SHAPE AND DIRECTIONALITY ON THE TRIBOLOGICAL BEHAVIOR OF POLYETHERETHERKETONE

3.1 Introduction

Among the challenges associated with modeling wear in polymers is the fact that a small change in the polymer's molecular structure can have a profound influence on the mechanical properties. The degree of crystallinity, presence of branching, and entanglement density will all influence the viscoelastic behavior of the polymer. Unlike metals that plastically deform because of dislocation movements, polymer deformation requires chains to slide, stretch, and orient themselves in the direction of the applied stress. This reorientation phenomenon will result in strain hardening until individual chains are stretched and rupture at their ultimate stress. During wear, chain orientation has been speculated to produce significantly different results depending on sliding direction. Ultra high molecular weight polyethylene (UHMWPE) is known to demonstrate much greater wear when exposed to cross shear motion compared to unidirectional sliding [24, 25]. An early indication of this effect was because of the observation by Charnley that polymer bearing surfaces in orthopedic joints exhibited far greater wear *in vivo* than seen in laboratory unidirectional pin-on-disk wear tests [26, 27]. Wang et al. showed that a wear simulator which modeled the motion of a joint resulted in two orders of magnitude greater wear than linear reciprocating tests [24]. The vast difference in wear observed was attributed to an orientation strengthening that occurs during linear motion and an orientation softening as a result of multi-directional wear [4]. This phenomenon has been verified experimentally as well as theoretically.

Scanning electron microscope (SEM) inspection of the plasma etched wear surface of UHMWPE has shown that the surface is stretched and crystal structure becomes oriented anisotropically [4]. Wang et al. proposed that this structural anisotropy promotes rupture between oriented chains. It was suggested and later proven [28] that low wear could be achieved by preventing this molecular reorganization through irradiation crosslinking [29]. Sambasivan showed that UHMWPE chains align parallel to the sliding direction by measuring the X-ray absorption spectra of the worn pin surface. Wear was believed to result from fracture of the unaligned loose chains [30]. When the strain energy effects of softening and orientation are accounted for, wear models have been able to accurately predict wear as a function of cross shear [31]. Irrespective of the underlying molecular dynamics, advances in UHMWPE bearing surfaces of implanted artificial joints have been made from knowledge of chain orientation during wear. However, techniques applied to UHMWPE to restrict chain orientation and improve wear performance may not be practical or possible in all polymers.

The molecular structure of polymers and its effect on friction and wear was first studied by Pooley and Tabor [32]. The low friction (COF <0.1) and material transfer behavior of polyethylene (PE) and polytetrafluoroethylene (PTFE) are a result of a smooth molecular profile and is independent of the crystallinity. The introduction of bulky side groups was shown to affect this behavior and it was believed the side groups prevented chains from orienting themselves into a smooth surface [32]. Poly(ether-ether-ketone) or PEEK is an aromatic-backbone semicrystalline polymer belonging to the polyaryletherketone (PAEK) family of thermoplastics. In wear applications, friction

is relatively high (COF ~0.3) but the polymer is capable of forming a protective tribofilm. Unlike polytetrafluoroethylene (PTFE) that forms a film due to its layered lamellae structure [33], the exact mechanism for PEEK transfer films is unknown. The formation of a transfer film is regarded to be integral in PEEK wear resistance. The film's rheological behavior, cohesiveness, and adherence to the substrate will all determine how effectively it can protect the bulk polymer from wear [34]. Surface roughness has been found to be a governing factor in PEEK wear and its relation to transfer film has been widely studied. Ovaert investigated the effects of counterface roughness on PEEK and found a minimum in wear occurred at roughness of 0.15μm [17]. At roughness below this, debris morphology changes indicating a difference in wear mechanism. Wear in polymers can generally be categorized in terms of adhesive, abrasive, and fatigue wear [12]. Adhesive wear implies that the polymer becomes bound to the underlying substrate and debris is generated during the shearing of the junction. Abrasive and fatigue wear however depend on hard asperities removing material from the softer bulk polymer through plowing and subsurface cracking respectively. In theory, development of a transfer film will protect the polymer from wear by covering sharp surface features. Additionally, since the film's modulus better matches the bulk polymer, subsurface stresses will also be reduced. Despite the general acceptance that transfer films are key in reducing PEEK wear, no clear understanding of an underlying mechanism for their formation exists. In polymer wear, it is believed that film formation is initiated by the mechanical removal and entrapment of debris by asperities. It has been suggested that when the counterface is excessively smooth, wear in polymers is

accelerated since there is a lack of transfer film generating surface features [1]. PEEK wear has also been observed to depend on the sliding direction relative to the surface roughness direction. Friedrich et al. observed wear to be more sensitive to increases in surface roughness when sliding was parallel to the roughness orientation and attributed it to a lack of transfer film formation [5]. Similarly, Ovaert observed the inability of PEEK to form continuous transfer films when surface roughness was angled relative to the sliding direction [35]. However, the vast majority of wear investigation of PEEK as it relates to transfer film generation has employed a pin-on-disk configuration where only unidirectional sliding is studied.

In this study, two grades of PEEK that differed in molecular weight were investigated using various sliding path shapes and directionalities to determine a relationship between wear and sliding orientation. A pin-on-plate tribometer was built that is capable of producing both linear and circular reciprocating paths. The experiment was designed so that sliding speed, distance, and calculated contact pressure were duplicated for circular and linear wear paths. In addition to wear, metrics were developed to objectively characterize and compare transfer film thickness and continuity between tests in order to help explain how PEEK wear is dependent on transfer film formation.

3.2 Materials and Methods

3.2.1 Materials

Samples from two different grades of PEEK material from the same supplier were used in this experiment. Identity of the supplier and grades has been withheld due

to contractual obligations to the sponsor of the work; however, mechanical and morphological properties of the materials were measured and are reported below. Samples were injection molded and finish machined into various geometry test specimens. The materials are graded according to their viscosity, which correlates directly to molecular weight M_w. Therefore, the selected grades 'L' and 'H' represent samples of low and high molecular weight, respectively. Gel permeation chromatography (GPC) was used to measure molecular weight and polydispersity index (PDI), and the results are shown in Table 2. Additionally, the degree of crystallinity was found through differential scanning calorimetry (DSC) and viscoelastic properties were found using dynamic mechanical analysis (DMA). These properties are also reported in the table.

Table 2. Compilation of morphological (weight average molecular weight, Mw, and polydispersity index, PDI, and crystallinity) and viscoelastic data (storage and loss moduli) for the two PEEK grades used in the study.

Sample	Mw	PDI	% crystallinity	Storage Modulus (GPa)	Loss Modulus (MPa)
L	66200	2.62	48	3.41	60.5
H	114362	3.11	42	3.11	69.4

3.2.2 Wear Testing

Volumetric wear was measured by determining the volume of material lost during wear testing. For this work, a tribometer with two axes of motion was constructed using two programmable linear stages (Aerotech). The tribometer allows for sliding of pin specimens against planar counterfaces under an applied normal load along a specified wear path and sliding velocity. Wear pins were loaded against counterfaces using

pneumatically controlled actuators and the tribometer was programmed to move in a specified path. Counterfaces were surface ground so the roughness was oriented in a single direction. This means that a circular path would result in a continuously changing orientation of surface roughness relative to the pin direction of motion. The goal of this experiment was to determine if wear path shape has a significant effect on wear in PEEK. With all other parameters fixed, a difference in wear would indicate that a multi-directional wear path influences PEEK differently than unidirectional motion. Additionally, it was desired to know if reciprocating motion will result in different wear behavior than an overlapping motion. To investigate this, four different wear paths, shown in Figure 9, were programmed so that an average velocity of 0.2 m/s was achieved. The total wear path distance of 2 km for an individual pin was the same for all four paths. These paths were selected so the influence of both multidirectional motion and reciprocating motion could be studied. Circular configurations were programmed to have a radius of 10 mm and were run for 32,000 cycles (approx. 2km sliding distance) in order to ensure steady state wear was reached. However, the circular paths studied differed in their velocity profile and/or directionality. A constant velocity circular (CVC) path involved a constant 0.2 m/s. However, in order to produce a reciprocating circular (RC) path, motion had to come to a complete stop and accelerate after each pass. The acceleration after each stop was set to 3 m/s^2 in order to achieve an average velocity of 0.2 m/s for the test. Similarly, a variable velocity circular (VVC) test configuration was used that also accelerated at 3 m/s^2; however, motion overlapped in the same direction after each pass rather than reciprocate. In order to study the effect of uni-

directional sliding, a linear reciprocating (LR) motion was used. Although the shape profile differed from the circular tests, acceleration and average velocity were identical to the (VVC) and (RC) tests. For the circular wear path, the angle between the direction of the pin motion and the counterface roughness direction was constantly changing. The linear reciprocating motion was set at an angle of 45 degrees relative to the counterface roughness direction. Thus, over the entire wear circuit, the wear pin was exposed to the same average surface roughness despite differences in wear path.

Testing was conducted using applied loads of 34 N (low) and 160 N (high), which resulted in Hertzian calculated pressures of 1.1 MPa and 5.1 MPa, respectively. Hardened D2 tool steel counterface plates (HRc 56.6 measured) were ground so that roughness was oriented in one direction with a measured roughness Ra of 0.5 μm. The loss in wear pin mass was recorded and the reported density of the respective PEEK materials was used to calculate volumetric wear. Wear testing followed a full factorial experimental plan with factors including normal load, polymer molecular weight, and wear path. For the wear tests using paths a, c, and d, a total of four pins of each material were tested in randomized order to account for statistical variation. A follow up test was conducted with eight replications for the circular reciprocation (c) and variable velocity circular (b) paths at a contact pressure of 5.1 MPa. This was done in order to further investigate the effects of overlap of the wear path under the same velocity profile as reciprocation.

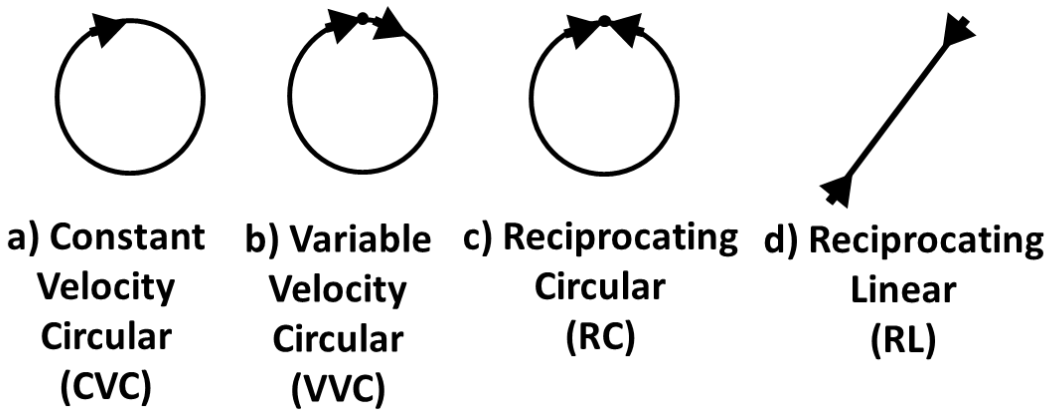


Figure 9. Wear path configurations used during the 2km sliding experiments. The CVC condition a) moved at a continuous velocity 200 mm/s for the first experiment. The paths in b,c,d accelerated at 3 m/s^2 after stop to achieve 200 mm/s average velocity.

3.2.3 *Transfer Film Measurement*

It is commonly reported that in order for a transfer film to protect against wear it should be continuous and cover a majority of the surface. In this work, a quantifiable comparison was made between the films formed during variable velocity circular (VVC) and reciprocating circular (RC) motions. Using Image-J software, pictures of films were converted to 8-bit images and the light threshold was set between 165 and 250 as shown in Figure 10. The light threshold was adjusted to make only the film visible in the foreground. The film area was calculated and compared with a hypothetical area of total film coverage. For a 6.35mm pin moving in a 20mm diameter circle, a film that covers 100% of the surface should have an area of 398.9 $mm^{2.}$

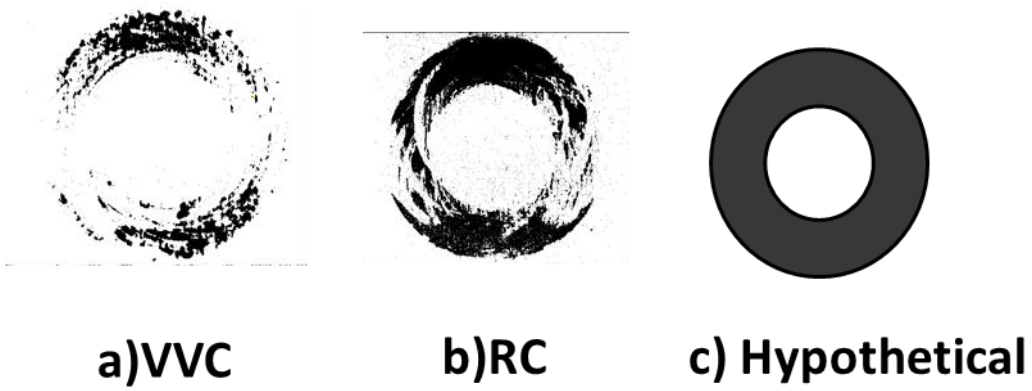


Figure 10. Area coverage measurement of transfer films using Image-J software.

Transfer films were also characterized using the distribution of film heights measured with a white light interferometry (WLI) based profilometer (Zygo). A three dimensional data map was produced, shown in Figure 11.a, and exported as a data file. Measurements were taken along the wear path at locations where sliding was perpendicular to the surface roughness orientation of the counterface, as shown in Figure 11.b. This was done to compare films formed under the same surface roughness conditions. In order to get a representative measurement of the entire transfer film at a particular sliding direction, eight measurements zones were analyzed. Therefore, the film height distribution represents a 0.7mm by 4mm area of transfer film. Data analysis was performed in Matlab in order to characterize the distribution of surface heights. It can be seen in Figure 11.c that there are two modes, which both closely follow a Gaussian distribution. In order to quantify the mean and standard deviation of the discrete data, a maximum likelihood estimation (MLE) was used to calculate a probability density function (PDF) for the distribution. The mathematical representation for the estimated PDF is shown in equation (1).

$$f(x; p, \mu_1, \mu_2, \sigma_1, \sigma_2) = (p)\frac{1}{\sigma_1\sqrt{2\pi}}e^{-\frac{(x-\mu_1)^2}{2\sigma_1^2}} + (1-p)\frac{1}{\sigma_2\sqrt{2\pi}}e^{-\frac{(x-\mu_2)^2}{2\sigma_2^2}} \qquad (1)$$

The PDF is produced under the assumption that the data represents a mixture of two normal PDFs, represented by each exponential term in (1). The function is dependent upon the percent mixture of each normal PDF (p) as well as the respective means (μ) and standard deviations (σ). When given starting points for the mean, standard deviation, and percent mixture of the two PDFs, a built in Matlab function performs iterations until it converges at a solution for the function f(x). The solution for the PDF parameters can then be used to characterize the relative film height and standard deviation. As shown in Figure 11.c, the leftmost mode reflects the ground surface roughness of the steel counterface and the rightmost mode indicates the height distribution of the transfer film. The white light interferometer quantifies height by identifying birefringence peaks as it vertically scans (40μm) the focal plane. During data processing, the heights are centered about zero and the relative distance between the plate mean (μ_1) and film mean (μ_2) are used to measure the film height.

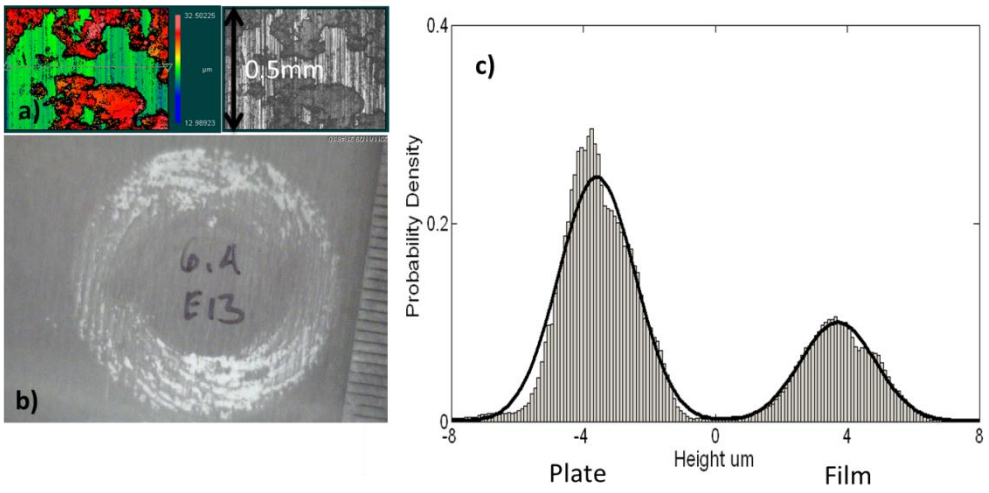


Figure 11. Transfer film characterization method using profilometer data.

3.2.4 Wear Surface and Transfer Film Imaging

Images of both wear samples and counterfaces were taken in a JOEL-6400 scanning electron microscope (SEM), and were prepared using a light sputter-coating of gold-palladium. Sections of wear pins were cut with a diamond saw, and then imaged in secondary mode with an accelerating voltage of 15keV. In order to fit the counterfaces in the SEM, samples were cut using an electron discharge machine (EDM) and were washed in acetone prior to coating. The transfer films were imaged with an accelerating voltage of 15keV. Images were taken at location representing sliding perpendicular to surface roughness. The primary objective of this work was to understand how transfer film is deposited when sliding changes direction. Therefore, only the high molecular weight samples ('H') exposed to variable velocity circular (VVC) and reciprocating circular (RC) motions were examined in the SEM.

3.3 Results

3.3.1 Wear

The results from all four wear test motion profiles of the two PEEK grades are plotted in Figure 12 for the calculated contact pressures of 1.1 and 5.1 MPa respectively. It should be noted that the sample sizes for (RC) and (VVC) at 5.1 MPa differ from the other groups. A follow up experiment was performed at these conditions to provide better statistical accuracy and therefore sample sizes are (n=12) and (n=8) respectively. Interestingly, despite the differences in molecular weight and contact pressure, the same general trends exist between the different wear paths. In the experiment, the sliding velocity and distance were kept constant so any differences seen in volumetric wear are attributed to the differences in motion. In all cases, the lowest wear resulted from reciprocating linear motion (RL), but the degree of difference depends on the molecular weight and pressure conditions. Tukey post-hoc analysis was performed on the wear data grouped by molecular weight and pressure as shown in Figure 12. In the plots, bars that are connected by roman numerals cannot be said to differ significantly with 95% confidence. At the 1.1 MPa pressure setting, the wear path has no effect on the high molecular weight sample, but is significant for all low molecular weight paths. However, with increasing pressure both samples differ significantly with respect to reciprocating motion. This is again most pronounced in the low molecular weight samples where all groups that differ do so with 99.9% confidence ($p<0.001$). Although the high molecular weight wear data does not appear to depend entirely on reciprocating, it should be pointed out that the (VVC) and (RC) paths were tested with a higher sample

size and are less influenced by error. The Tukey test between these two groups says they are significantly different ($p<0.001$) and therefore indicates that an explanation for why a reciprocating path produces the lowest wear is needed.

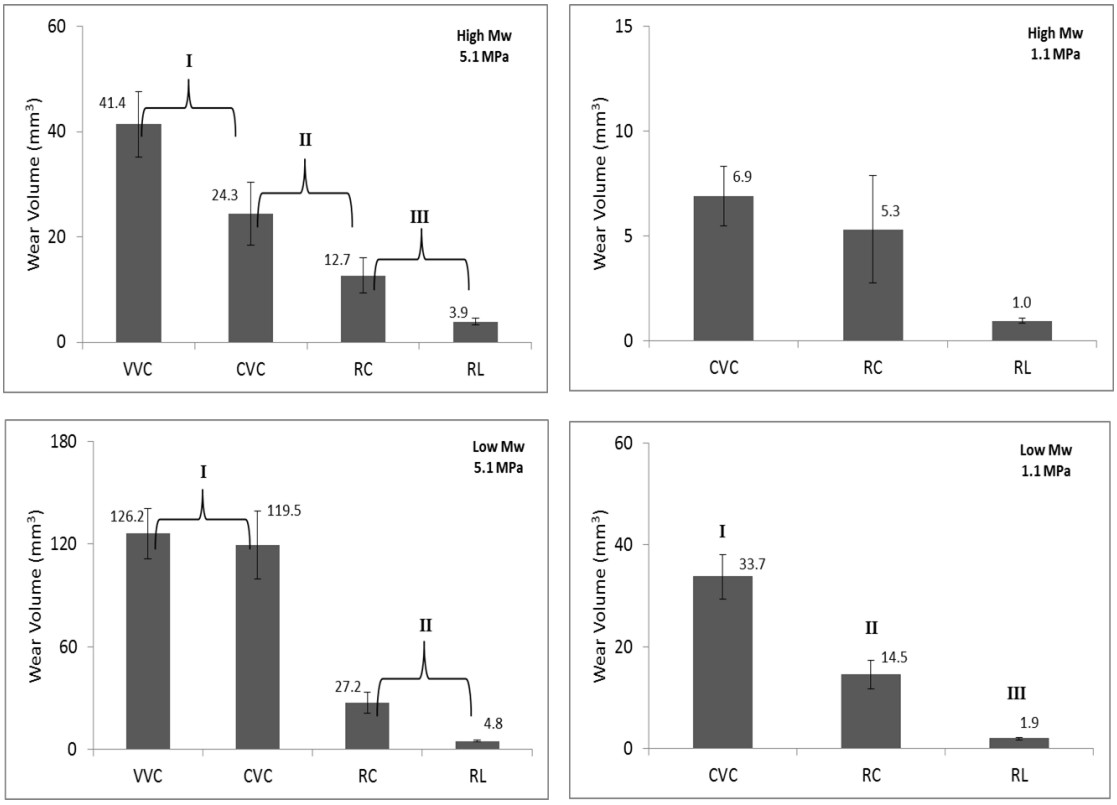


Figure 12. Wear volume data for all combinations of pressure, molecular weight, and path. Groups not connected by brackets are significantly different ($p=0.05$). Sample size ($n=4$) with the exception of VVC and RC in a), c).

3.3.2 Transfer Films

Visually, it is apparent that a qualitative difference exists between films produced with reciprocating circular path (RC) and those that result from an overlapping (VVC) path as seen in Figure 13. Also, both circular wear paths (VVC) and (CVC) produce similar films despite different velocity profiles. It is reasoned that the film formation is dependent on whether the wear path reciprocates or overlaps and only the (VVC) condition was analyzed. Figure 13 shows the resulting films from high molecular weight samples tested at both low and high contact pressures and with the (VVC) and reciprocating (RC) wear paths. Comparing the films, two main differences exist. First, when contact pressure increases, the amount of material deposited on the counterface appears to increase as well. This effect is most prominent in the reciprocating films Figure 13.b and d. Secondly, films produced with the overlapping (VVC) wear condition appear qualitatively lumpier and more discontinuous even at low contact pressure. In particular, the reciprocating film in Figure 13.d has a smooth uniform appearance. It is also important to note that the same qualitative trends were seen in films produced with the low molecular weight samples. The calculated area coverage for high molecular weight samples under contact high pressures (5.1 MPa) confirms that there is a quantifiable difference between the wear paths as well. The mean coverage from the overlapping (VVC) and reciprocating (RC) tests are 19% and 40%, respectively.

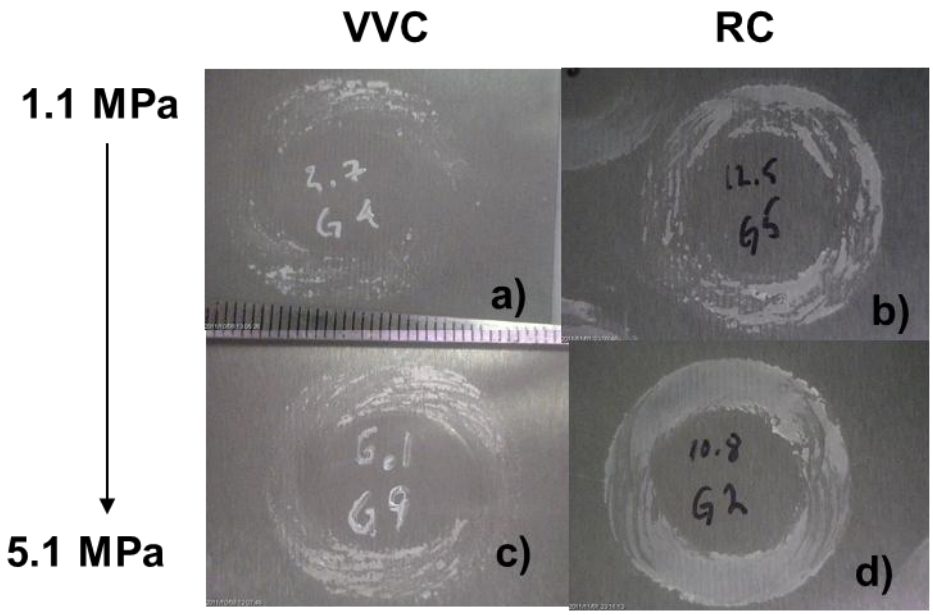


Figure 13. Transfer film images for VVC and RC at low and high contact pressures.

Similarly, analysis of the film height data from the same tests shows that reciprocating films are both thinner and have a more uniform distribution of heights. The probability density functions for the (VVC) and reciprocating (RC) conditions, shown in Figure 14, give quantitative differences between the film heights. A mean value for the film height with respect to the asperity heights can be represented by the difference between the PDF plate and film heights μ_2-μ_1. Data from the eight (VVC) wear tests indicate that on average the film has a height of 6.65μm and a standard deviation of 1.52μm. The data from the reciprocating circular (RC) paths however are nearly half this with a film height of 3.15μm and a standard deviation of 0.53μm. It should also be noted that the measured standard deviation for the plate asperity heights are nearly identical for both data sets (~1μm).

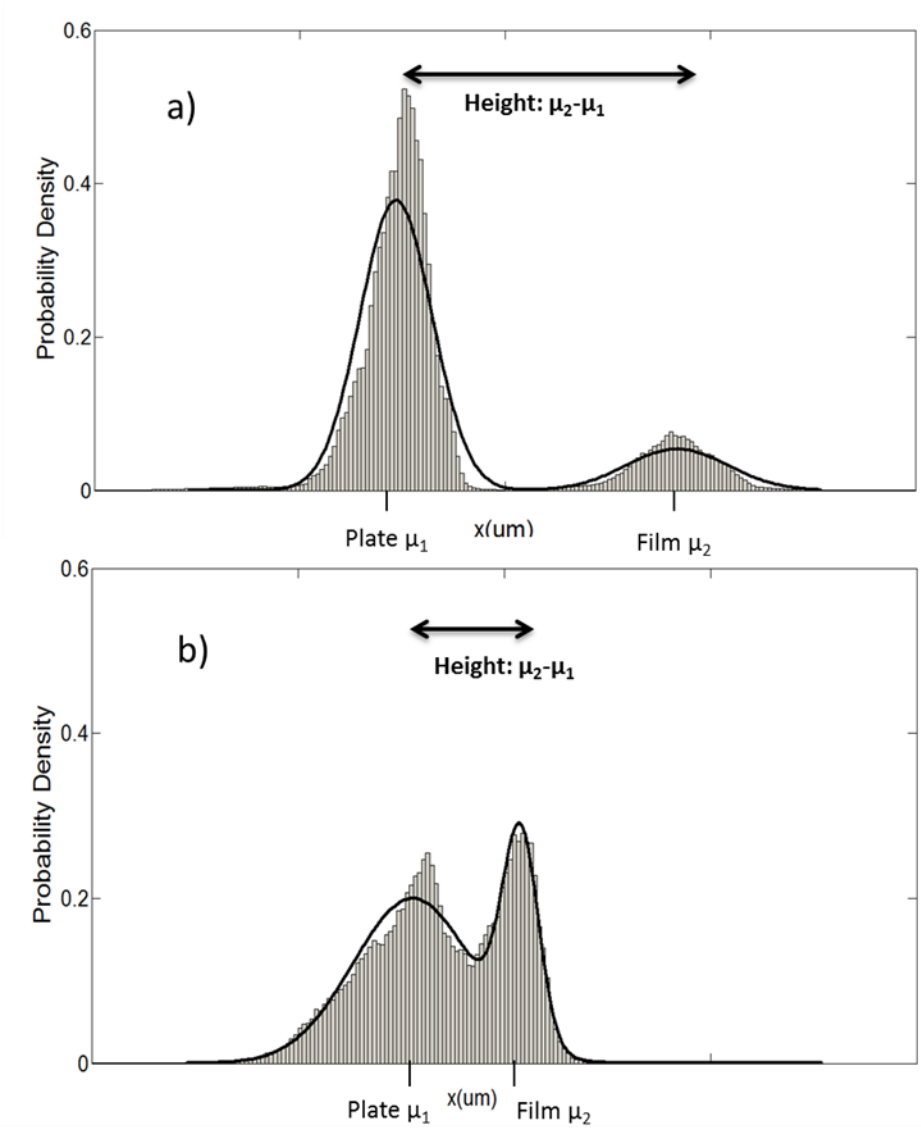


Figure 14. Transfer film height distributions. a) Film produced by (VVC) motion with height 6.5µm. b) Film produced by (RC) motion with height 3 µm. X-axis tick marks on the top of the each figure are separated by 5µm.

3.4 Discussion

It is generally assumed that the presence of a transfer film during polymer wear protects the bulk material from the harder asperities. However, it is not fully understood

what types of films are able to reduce wear and under what conditions these films form. During this study, it was found that quantifiably different films form as a result of changes in sliding direction for PEEK polymers. With all parameters fixed lower wear results from reciprocated sliding. When the sliding motion overlaps in a circular configuration, a lumpy discontinuous film is deposited. However, changing direction results in thinner, more uniform and more continuous transfer films. The rationale for why these differing films form can be explained by observation of film deposition on asperities. The scanning electron microscope (SEM) images of wear tracks on select counterfaces are shown in Figure 15. Observation of the films shows that when the pin slides without changing direction, material is deposited in a much different manner. The resulting film is made up of many small islands that align themselves with the surface roughness direction. A change in direction however produces what appears to be a continuous sheet of film with very little void space. The film also takes on a corrugated texture with ridges aligned with the direction of surface roughness as seen in Figure 15.c. These observed differences give insight into how the transfer films possibly form and how material is removed from the bulk.

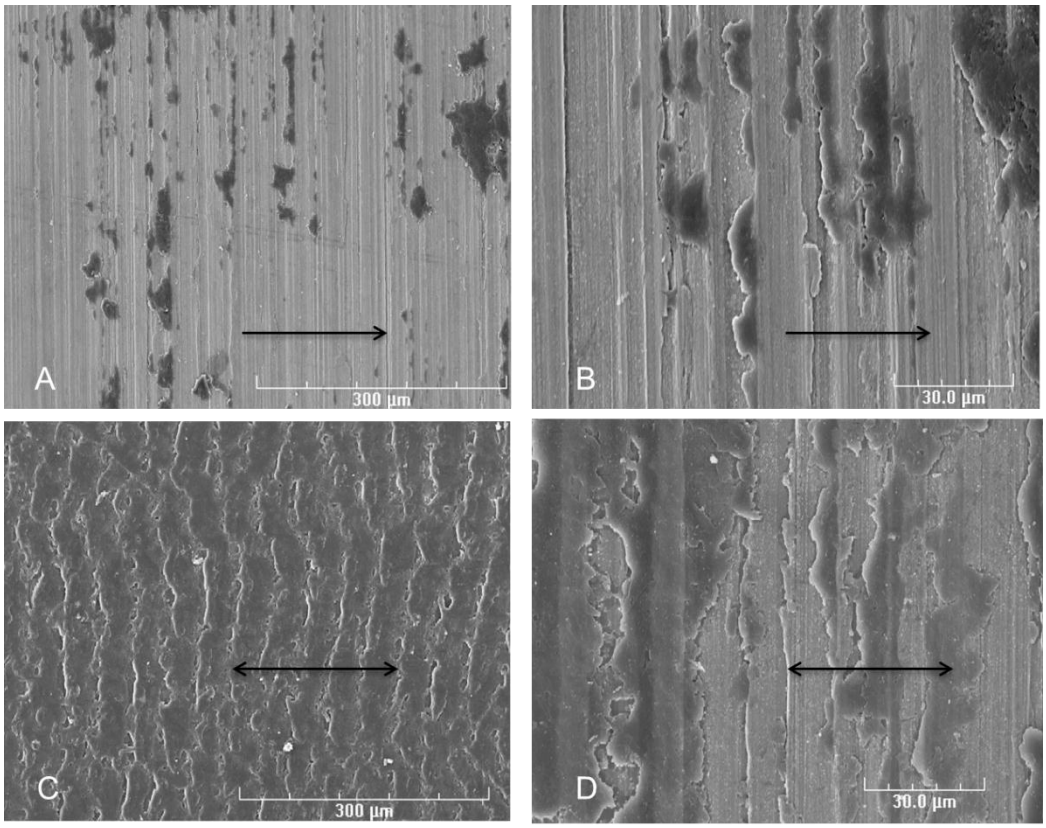


Figure 15. Scanning electron microscope (SEM) images of PEEK transfer films deposited on hardened D2 steel counterfaces. Arrows indicate the direction of sliding relative to the surface roughness.

Material tends to deposit on one side of asperities in overlap sliding as shown in Figure 15.a and b. As the pin traverses the counterface, it can be surmised that the leading edge of the asperity penetrates the bulk polymer and removed material collects on the front flanks. The trailing edge of the asperity is left exposed because it is unable to make contact with the bulk. However, this does not explain why material does not deposit on the front of every asperity and why some material deposits over the top of multiple asperities. In order to understand this, we need to consider the distribution of asperity heights and space between asperities. Although plates were all ground to a surface

roughness (R_a) of 0.5μm, the asperity height and spacing follows a Gaussian distribution. Within this range of heights, there is likely some critical height and spacing that deposited material cannot bridge. When an asperity of sufficient size is encountered, the removed material will pile up and agglomerate into large islands as shown in Figure 16. One large island has formed with a boundary clearly marked by the front edge of an asperity.

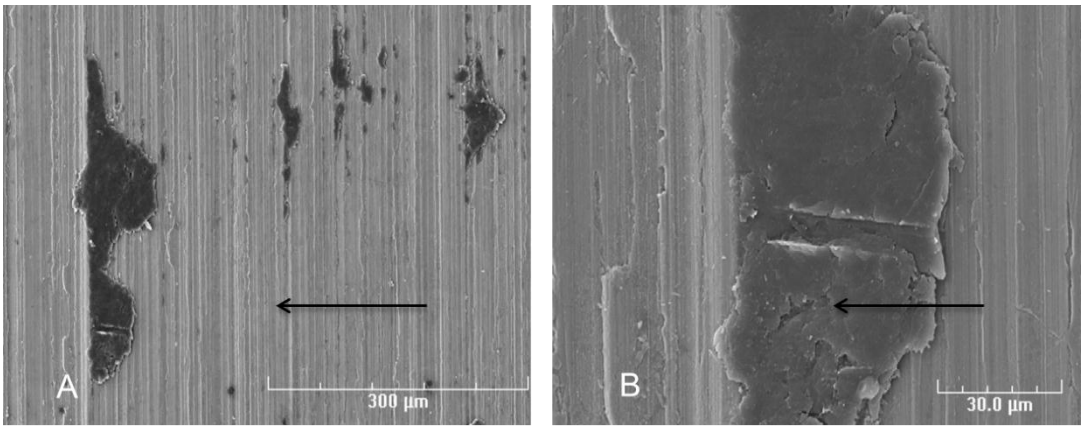


Figure 16. Scanning electron microscope (SEM) images of PEEK film trapped on the leading edge of an asperity. A) several large islands aligned with the asperities. B) 1000x image of the island in the lower left corner of A).

Theoretically, there is a height and spacing for asperities where every ridge can be filled by debris. In Figure 17.a, the asperities are evenly spaced and of the same height. As the pin moves over the counterface, each asperity penetrates into the bulk and plastically deforms the surface. Since the pin is able to contact all points, each leading edge will become covered with the entrapped debris. However, the trailing edge of asperities will remain exposed and will still be capable of abrading the pin. If the pin motion changes direction, the opposing edges can then be covered. The corollary to Figure 17.a is a

counterface with ridges of varying heights and spacing. When the counterface is made up of tall peaks, shown in Figure 17.b, the pin surface is unable to contact each asperity. If the asperity is of sufficient height, it will plastically deform the pin surface such that it does not make contact with subsequent asperities. Wear debris collects on the face of these taller peaks, but a continuous transfer film does not form. Similarly, large spaces between ridges will prevent material deposition on every asperity shown in Figure 17.c. Although the pin can be worn by all peaks, the space between the ridges is too large to entrap debris.

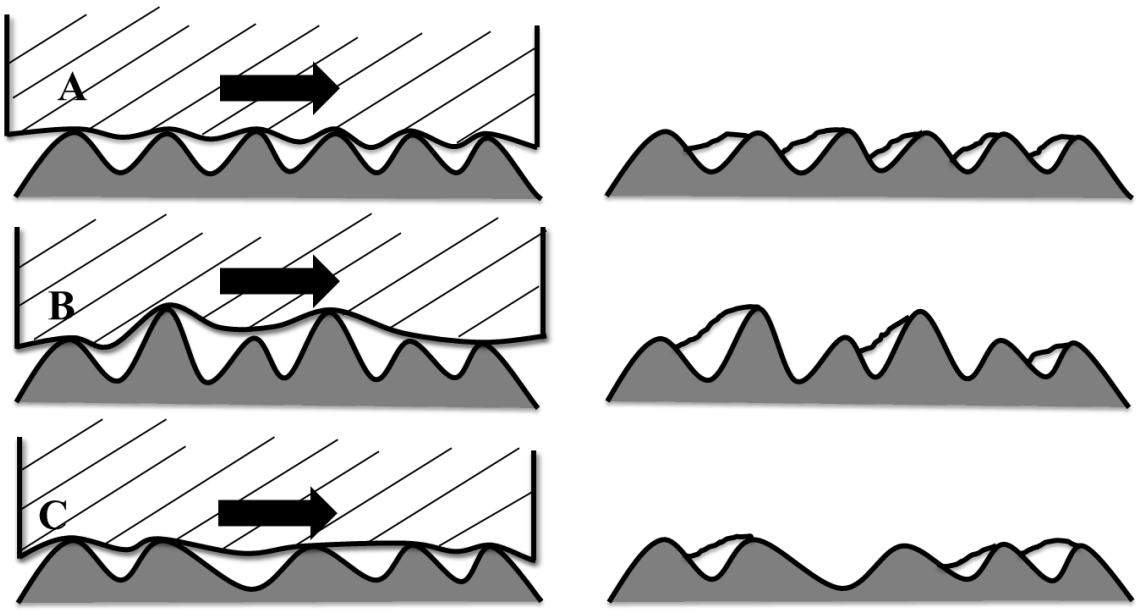


Figure 17. A theoretical illustration of how asperity height and spacing will influence material deposition during sliding. A) Uniform distribution of heights and spacing. B) Influence of tall asperity peaks. C) Influence of large gaps between asperities.

The distribution of asperity heights and spacing does not explain why a thin continuous film forms with a reciprocating wear path and why lower wear results. To understand

this, we need to understand the wear mechanisms involved. Abrasive wear refers to material removal that is the result of a softer material rubbing against a hard rough surface. This appears to be the dominant mechanism for the wear path that overlaps with each pass as seen in Figure 18.c and d. The worn pin surface is scored and large craters develop from debris being continuously removed from the bulk. It is believed that a transfer film can protect against abrasive wear because the film's modulus more closely matches that of the polymer surface. As worn debris is deposited on the edges of asperities, fewer and fewer hard asperities make contact with the pin. At some point, the pin surface begins to contact the already deposited material and pull it over the top of each ridge. When the wear path reciprocates across both sides of asperities, a film can be drawn out as a continuous sheet over all asperities. This drawing out process manifests itself on the pin surface seen in Figure 18.a and b. With the exception of stuck debris, the reciprocating wear surface has a smooth topography absent of the scratches and craters seen during abrasive wear. Additionally, fibrous sheets appear to emanate from the surface of the pin. It is unclear whether these features originate from the bulk polymer or are drawn out from already deposited material. However, the drastic difference seen in the pin surface indicates a transition away from abrasive wear associated with the different wear path configuration.

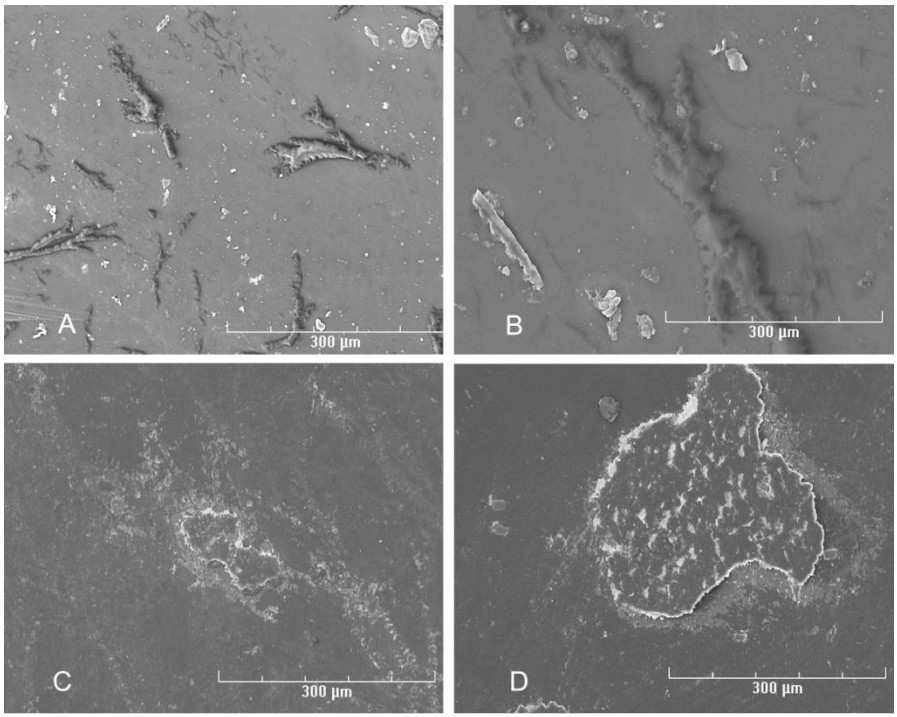


Figure 18. Scanning electron microscope (SEM) images of the worn PEEK pins after 2km sliding wear test for two different motion paths. A),B) Circular reciprocating motion. C),D) Circular overlap motion

3.5 Conclusions

The following conclusions were drawn based on the results of this study:

1. When all other parameters are kept fixed, there is a statistically significant difference in the wear behavior of PEEK depending on the motion profile. At a contact pressure of 5.1 MPa, reciprocating motion results in lower wear with $p<0.001$.

2. A quantifiable difference is observed in the PEEK transfer films deposited for circular wear paths depending on whether or not the motion changes direction with each pass. Films formed as a result of a circular overlapping path are observed to be lumpy

and discontinuous relative to those of a circular reciprocating path. These differences are measurable in terms of the film's percent coverage and distribution of heights.

3. Lower wear is associated with a reciprocating wear path as a result of a transfer film that is able to cover hard rough asperities. Scanning electron microscope (SEM) inspection of the counterfaces shows that debris tends to collect on one side of an asperity for motion that overlaps in a single direction. If the pin is able to reciprocate, the trailing edge of asperities can be covered and prevented from making contact with the bulk.

4. The PEEK wear pin surfaces show a drastic difference in topography associated with a thin continuous transfer film. When the transfer film sparsely covers asperities, the pin surface is deeply scored and cratered indicating abrasion from the hard rough asperities.

3.6 Acknowledgement

The authors would like to thank the members of the consortium for Advancing Performance Polymers for Energy AppLications (APPEAL) for providing the financial support and PEEK materials used in this study.

4. CONCLUSIONS AND CONSIDERATION FOR FUTURE RESEARCH

4.1 Summary and Conclusions

This research was undertaken in order to gain a fundamental understanding of the relationship between wear and transfer film formation in polyetheretherketone (PEEK) polymers. It was found that contact pressure and molecular weight have a pronounced effect on wear. With statistical significance, lower contact pressure and higher molecular weights result in the lowest wear. Additionally, the differences in mechanical properties that arise from different manufacturers were investigated as to how they contribute to wear. When the pressure is low (1.8 MPa), there is not a statistical difference in wear between the two manufacturer's material of comparable molecular weight. However, a difference in wear behavior is observed when pressure is increased (3.9 MPa). The explanation for this change in behavior is not fully known, but may arise from the viscoelastic properties. Dynamic mechanical analysis suggests that there is a difference in the room temperature storage and loss modulus between the two manufacturers. It is not fully understood how this relates to wear, but it implies that a full spectrum of mechanical properties needs to be considered when reporting wear data for a material grade.

Transfer film formation was also found to be both qualitatively and quantitatively related to sliding direction. Under conditions of multi directional sliding, where the pin continuously overlaps in the same direction, transfer film appearance changes with relative direction to asperities. Film appears to be thickest at locations sliding

perpendicular to the roughness direction and thinnest when sliding parallel to roughness. It is possible that there is some angle at which an asperity is unable to remove material from the bulk. This directional dependence on wear and transfer film formation was found to be significant when sliding direction changed with each pass. A wear path that reciprocated back and forth in a single direction was found to produce significantly lower wear than one that reciprocated in a multi-directional pattern. Additionally, reciprocating produced thinner and more continuous films that protect the bulk polymer from wear by hard rough asperities.

4.2 Considerations for Future Research

Although a great deal of fundamental knowledge on the wear behavior of PEEK was gained in this study, several new questions were uncovered that are worth exploration. Wear is known to depend on a multitude of parameters outside of the molecular weights, contact pressures, and sliding directions studied. Typically, wear behavior of polymers is graded in terms of the pressure velocity product (PV). However, the pressure and velocity will influence wear both independently and synergistically. Therefore, further study on how various grades behave at different pressures (P), velocities (V), and combinations of PV would be of significant merit. Detailed knowledge of how these parameters interrelate to material properties would allow polymers to be tailored to specific applications. The wear path parameters could also be related to wear and optimal as well as problematic configurations for PEEK could be identified. A fundamental question that remained unanswered during this study is why a unidirectional linear reciprocating (LR) path resulted in the lowest wear.

Speculation still remains as to whether PEEK has the ability to orient its chains in the direction of maximum shear. Analysis of the worn pin surfaces through chemical spectroscopy would give insight into how polymer chains are stretched and oriented during different wear conditions. Additionally, with increasing pressure and velocity the thermal contributions from friction are believed to become increasingly important to wear. Although the frictional forces were recorded during each experiment, measurement drift in the sensor prevented any reliable data from being recorded. Instrumentation to accurately record friction throughout the test would give deeper insight into the transfer film formation mechanics. A method to measure the temperature of the polymer plate interface would help explain how the polymer mechanical properties vary with test conditions. This can be accomplished through in-situ monitoring of the interface with a pyrometer. Furthermore, analysis of the chemical composition of the wear debris and worn pin surface would allow for speculation as to what temperatures were experienced by the sample. Although these ideas are not included in this study, groundwork is currently underway to allow for this deeper investigation.

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